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Tribofilm Formation and Characterization of Lubricating Oils with Biofuel Soot and Inorganic Fluorides

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Abstract

A series of tribological experiments have been conducted to characterise and study the formation of tribofilms derived from TiF_3 and FeF_3 catalysts impregnated in soot-contaminated lubricants. Tests were conducted with a Titanium and an Iron inorganic fluoride based additives on an end-face tribometer. A systematic approach was used to establish basic wear data producing a detailed design methodology for the development of optimized engine oil that is resilient to soot contamination. Results showed that inorganic fluorides reduced friction and wear in the specimen contaminated lubricants. With the best results observed when TiF_3 was used. There were also indications that the frictional process, when coupled with the fluorides induced a structural change in the soot particles within the contact zones, contributing to the improved tribological performance. The key contributors to the formation of robust tribofilms were adsorption and tribo-chemical reactions. The better tribological response leads to a method for the design of engine lubricants to mitigate against the effects of soot contamination.

Keywords: Soot, Nanoparticles, Tribofilm, Tribochemistry, Lubricating oil

Research Highlights

- Tribological properties of inorganic fluoride derived additives investigated
- TiF_3 and FeF_3 dispersed in a liquid paraffin base Oil and formulated lubricant
- Additives reduced friction and wear in soot contaminated lubricant
- Fluorides assisted in the formation of robust tribofilms, TiF_3 produced best results
- Friction coupled with additives changed the structure of the soot particles

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1. Introduction

Biomass pyrolysis fuel is receiving increasingly more attention because of several potentially beneficial characteristics that include a low sulfur content and environmental-friendliness. Refined biomass can be used to prepare emulsified biomass fuel (biofuel), which has been used in diesel engines [1-3]. When used as a combustible fuel, soot is generated, and this can have a negative effect on the tribological surfaces within the engine. Eliminating biomass fuel soot particles (biofuel soot, BS) in diesel engines is extremely difficult. Soot particles can contaminate lubricating oils within the sump through blow-by gases, which can be further worsened by exhaust recirculation systems [4, 5]. Engine soot particulates can increase the kinematic viscosity and acid number of a lubricant, as well as promote the appearance of oily slurry in the engine sump, which combined leads to a shortened oil life [6, 7]. Moreover, soot particulates can result in an increased wear of critical components, thus indicating the importance of investigating the tribological impact of BS contamination of lubricating oils.

Soot contamination is a serious issue that has been extensively investigated the engine and lubricant industry and academia. Studying soot however is challenging not least because the collection of soot particles from the engine sump is a time-consuming and laborious task. Researchers therefore tend to simulate the soot by using simulated particulates generated from, for example, a diffusion flame or carbon black. These substitute engine soot particles can then be used to study the effects of contamination on the lubrication properties of lubricating oils. However, the differences in the nanostructure, composition and surface functional groups among engine soot [8], carbon black [9] and flame soot [10, 11] are likely to result in morphological changes in a state of agglomerates in a lubricant [12], and so may result in a different tribological response of lubricating oils [13]. For example, in previous research, the graphite degree, composition and surface function group (-OH) content of BS particles were higher than those of commercial carbon black [14].

There have been many studies of the tribological mechanisms of soot particles in lubricating oils that have been conducted on a variety of different tribometers, with a variety of lubricants, soot contents and soot types. Green and Lewis [15, 16] used carbon black particles as a substitute for engine soot and presented abrasion effects and variations in the lubrication

conditions that determined the wear mechanism dominating in specific situations. Others studies also indicated that carbon black rapidly removed tribological films by abrasion [17]. Rounds et al. [18] postulated that the adsorption role mechanism of carbon black resulted in reducing antiwear components in lubricants. These studies indicate that a large number of different wear mechanisms can be observed when carbon black is as a substitute for engine soot when investigating the tribological behaviors of lubricating oils,. Antusch et al. [19] measured the mechanical properties of different soot particles and found that they were closely related to their reactivity and the amount of defect sites. George et al. [20] indicated that base stock and soot content were the most significant variables affecting wear. However, interestingly some researchers have found that low levels of soot particles can have a beneficial effect on the tribological performance of lubricating oils. Hu et al. [21] revealed that low levels (1 wt.%) of carbon black enhanced the antifriction properties of engine lubricating oils using a four-ball tribometer. Liu et al. [22] also indicated that soot (3 wt.%) in certain engine oils appeared to act as a friction modifier. Wei et al.[23] prepared candle soot and obtained similarly beneficial tribological results.

The structure and composition of BS particles are different to traditional diesel engine-derived soot particles because of the complicated composition of biomass fuels. There have been few studies to date that have investigated the tribological effect of self-prepared BS and low BS contamination levels on the tribological behaviors of engine oils. The effects of TiF_3 and FeF_3 catalyzing tribofilms in contacts lubricated with different lubricants has been investigated by Nehme [24-26]. They focused on the investigation of the efficacy of TiF_3 and FeF_3 particles, along with polytetrafluoroethylene to zinc dialkyldithiophosphates (often referred to as ZDDP), in promoting the formation of robust anti-wear films, using a sliding ball-on-ring tribometer. Robust material transfer layers and tribochemically formed films are responsible for improving the wear resistance and friction reduction of engine lubricating oils [27]. Mourhatch and Swathe [28, 29] used different contact loads and performed several chemical characterization studies to differentiate between tribofilms of lubrication oils with and without FeF_3 . Parekh et al. [30] examined the chemical interactions between ZDDP and FeF_3 . A new chemical species was detected and was shown to be responsible for improved wear performance. TiF_3 and FeF_3 catalysts are both known to reduce gas emissions and promote ZDDP degradation [31], which could improve the antiwear and antifriction properties of engine oils, as well as reduce sulfur and

phosphorous levels.

At present, studies on the use of inorganic fluorides with low content BS contaminated Liquid Paraffin (BS-LP) and fully formulated engine oil are limited. Previous work [32] has shown that TiF_3 can promote anti-wear and anti-friction properties of carbon black contaminated-LP and CD SAE 15W-40 using a four-ball tribometer. This paper describes a study on the formation and characterization of tribofilms from TiF_3 and FeF_3 catalysts (0.5 wt.%) on the tribological behaviors of low-content (3 wt.%) BS contaminated LP and fully formulated engine oil (CD SAE 15W-40). A series of tribological experiments were conducted using an end-face tribometer to assess the tribological properties of 3 wt.% BS-contaminated LP and CD SAE15W-40 with and without 0.5 wt.% TiF_3 or FeF_3 . A systematic approach was used to establish basic wear data and then a detailed design methodology for the development of optimized engine oil that is resilient to soot contamination.

2. Experimental

2.1 Materials and sample preparation

Commercial diesel (number 0) was purchased from China Sinopec Corp. Crude biomass pyrolysis fuel was produced by a rapid pyrolysis process with rice husks, which were provided by the Key Laboratory for Biomass Clean Energy of Anhui Province, China. The composition and physicochemical properties of crude biomass pyrolysis fuel were analyzed, as shown in [33]. The main components include acids, alcohols, esters and aldehydes, ketones, sugars, and furans.

Emulsified biomass fuel was prepared by mixing refined biomass fuel (5 wt.%), diesel (93 wt.%), and Sp-80 emulsifier (2 wt.%) at a stirring speed of 1500 rpm and at 65 °C for 60 min. The BS was prepared using a soot trap, in which emulsified biomass fuel was burned at room temperature (approximately 25 °C)[14]. Fig. 1 shows the morphology and distribution diagram of the average particle diameter (APD) of the BS particles. In Fig. 1(a) the BS is agglomerated. Single particles presented graphite debris at their edges, as shown in Fig. 1(b) (red triangle). The inset diffraction pattern of the carbonaceous material also indicated the presence of a large amount of amorphous carbon. BS particles possess virtually indistinguishable perturbed graphitic or turbostratic internal structures [34, 35]. The distribution diagram revealed that the APD was approximate 37 nm.

Commercially available LP (Hengshui Diyi Petro-Chemical Co., Ltd.) and fully formulated engine oil (CD SAE 15W-40, China Sinopec Corp.) were used for this investigation. The LP with a simple composition was chosen in order to better analyze the tribological behavioral differences between the TiF_3 and FeF_3 . The CD SAE15W-40 oil was a low-grade engine lubricating oil that is frequently used in farmland tractors under extreme conditions in China. CD SAE 15W-40 oil was formulated including some additives such as Zinc Dialkyl Dithiophosphates (ZDDP), anti-oxidants, dispersants and so on. The physicochemical properties of the lubricants are shown in Table 1.

Commercially available TiF_3 and FeF_3 catalysts were both purchased from Alfa-Asia Tianjin Chemical Co. Ltd. The other reagents were all of analytical grade. LP oil samples were prepared with 3 wt.% BS, 0.5 wt.% TiF_3 , 3 wt.% BS + 0.5 wt.% TiF_3 , 0.5 wt.% FeF_3 , and 3 wt.% BS + 0.5 wt.% FeF_3 . The 3 wt.% BS was close to actual maximum engine soot contaminated lubricating oil. The BS and catalysts were dispersed uniformly with vigorous stirring for 2 hours assisted by ultrasonication for 30 min to reduce experimental deviation. The CD SAE15W-40 oil samples were prepared in the same manner.

2.2 Tribological and Analytical methods

Tribological tests were conducted on an end-face tribometer (HDM-20) manufactured by the Institute of Tribology, Hefei University and Technology, at ambient temperatures. The schematic diagrams of the friction pair of end-face tribometer are shown in Fig. 2. The top sample was a commercially available ductile cast iron (ASTM A536, HB = 164), which is commonly used to in piston rings and bearings parts. The inside and outside diameters of top samples were 30 mm and 22 mm, respectively. The disk sample was prepared using a grey cast iron (ASTM A48, $R_a = 0.385 \mu\text{m}$ and HB = 174), again commonly used as cylinder liners and bearings parts, the diameter and thickness were 53 mm and 4 mm, respectively.

Prior to the tribological tests, the top sample was polished in order to obtain a surface roughness (R_a) of $0.345 \mu\text{m}$ and to reduce experimental deviation. The test conditions were as follows, initially 50 N for 2 min then the friction and wear properties of the oil samples were analyzed at 1500 N and with a rotation speed of 294 rpm for 60 min. The contact pressure was approximately 1.12 MPa. All tribological tests were replicated three times to reduce experimental

deviations. For each test new samples were used. Qualitative and quantitative analysis focused mainly on the lower disk samples because of the complicated geometry of the top sample, as well as the mitigating the time-consuming preparation and machining processes required to prepare the upper sample for analysis. The tribological behaviors of the oil samples were assessed by variations in mass loss of the disk sample and friction coefficient, respectively. Mass loss was calculated as follows:

$$\Delta m = m_0 - m_1$$

where Δm is the wear mass loss (mg); m_0 is the initial mass of the disk sample (mg); and m_1 is the mass of the disk sample after the rubbing process (mg).

Scanning electronic microscopy coupled with energy dispersive spectroscopy (SEM/EDS, JSM-6490LV) was employed to investigate the morphologies and elements of the wear traces after the rubbing process. A surface profiler (Taylor-Hobson-6) was used to measure surface roughness (R_a) with appropriate magnification. To sufficiently clarify the wear and friction mechanisms of TiF_3 and FeF_3 catalyst materials in 3 wt.% BS-contaminated lubricants, X-ray photoelectron energy spectroscopy (XPS, ESCALAB259) was utilized to analyze the chemical element state of the tribofilm after the rubbing process. Raman spectroscopy (RS, LabRAM-HR; resolution = 0.6 cm^{-1} , scanning repeatability = $\pm 0.2 \text{ cm}^{-1}$, $\lambda_0 = 514 \text{ nm}$) was conducted to study the carbon species of wear traces. Finally, the disk samples were immersed into the lubrication oils with and without 3 wt% BS containing 0.5 wt% FeF_3 or TiF_3 at 70°C for 2 h. The surface elemental contents of the disks were detected by EDS analysis. These tests were aimed at clarifying the role of physical adsorption when FeF_3 or TiF_3 was added into both the LP and CD SAE 15W40.

3. Results and Discussion

3.1 Wear resistance and friction reduction

Fig. 3 shows the mass loss and average friction coefficient variations of 3 wt.% BS contaminated LP and CD SAE 15W-40 with and without 0.5 wt.% TiF_3 or FeF_3 . The mass loss of pure LP was 19.8 mg in Fig. 3(a). For 3 wt.% BS contaminated LP, mass loss was 30 mg, which indicated that BS promoted wear a trend in common with [15,16]. However, when 0.5 wt.% of the catalysts (TiF_3 or FeF_3) were added, mass losses decreased to 0.99 and 0.20 mg, respectively, which indicated that the fluoride catalysts enhanced the antiwear properties of 3 wt.% BS

contaminated LP. The addition of TiF_3 and FeF_3 in uncontaminated LP was also investigated. Mass loss was evidently decreased, which showed that TiF_3 and FeF_3 perform important functions in improving the antiwear properties of BS contaminated LP. Nehme also found that a TiF_3 / FeF_3 mixture was both beneficial in promoting anti-wear and friction reduction properties of lubricating oils including PTFE particles [31]. The results indicated TiF_3 and FeF_3 had positive role in restraining the degradation of BS contaminated engine oils.

Fig. 3(b) shows the variations in the mass loss of the disk samples lubricated with the CD SAE 15W-40 lubricant containing 3 wt.% BS with and without 0.5 wt.% TiF_3 or FeF_3 . The mass of the pure CD SAE15W-40 was 2 mg. As for the 3 wt.% BS contaminated lubricant, the obtained mass loss was 3.5 mg, an approximate 75% increase in comparison with that of pure lubricant. This finding indicated that BS degraded the antiwear property of CD SAE 15W-40. With the addition of 0.5 wt.% TiF_3 or FeF_3 in the lubricant, mass loss decreased to 0.7 and 0.9 mg, respectively. The addition of TiF_3 or FeF_3 into uncontaminated CD SAE 15W-40 was also investigated. In general, these results again proved that TiF_3 and FeF_3 catalyst materials contributed to improving the wear resistance of BS contaminated CD SAE 15W-40.

The average friction coefficient of LP with 3wt.% BS and 0.5.wt% TiF_3 was slightly lower than that of pure LP or LP+3 wt.% BS as show in Fig. 3(c). This indicated that TiF_3 can modify the antifriction property of LP. This result also can be proved by the average friction coefficient of CD SAE 15W-40 including 3 wt.% BS and 0.5 wt.% TiF_3 in Fig. 3(d). However, the FeF_3 did not contribute significantly to the improvement of the antifriction properties of CD SAE 15W-40, which was possibly ascribed to the final frictional products such as the iron oxides. It indicated that the TiF_3 was better than FeF_3 in the friction reduction property of lubricating oil contaminated 3wt% BS.

3.2 Surface analysis

The morphologies of the wear traces on the disk samples were analyzed using SEM/EDS to investigate how the BS particles promote wear. The surface roughness variations of wear zones lubricated with 3 wt.% BS-contaminated LP and CD SAE 15W-40 with and without TiF_3 or FeF_3 were characterized with the surface profiler. Fig. 4 shows the SEM images and surface roughness of the wear zones of disk samples lubricated with LP and CD SAE 15W-40. The initial surface

morphology of grey cast iron is shown in Fig. 4(a). Multiple textures, which were caused by the machining procedure, were observed on the surface. The initial surface roughness (R_a) of grey cast iron was 0.385 μm . For the samples lubricated with pure LP, debris appeared within the worn region. The White arrows shown in Fig. 4(b) represent small pits and delaminated regions. The R_a for the sample shown was 0.851 μm , suggesting that severe wear had occurred when lubricated with pure LP. For LP contaminated with 3 wt.% BS (Fig. 4(c)), numerous pits were observed and were ascribed to material ‘peel off’. Debris and delaminated regions also existed, and the R_a was 0.712 μm . In the case of added 3 wt.% BS + 0.5 wt.% TiF_3 , the pitting and delaminated regions disappeared (Fig. 4(d)), and a smoother surface was observed ($R_a = 0.398 \mu\text{m}$), which was caused by the formation of a tribofilm [36]. With the addition of 3 wt.% BS + 0.5 wt.% FeF_3 into LP, a smooth surface was observed, including smaller pits (Fig. 4(e)) that were filled with BS particles ($R_a = 0.335 \mu\text{m}$).

Fig. 4(f) shows the surface morphologies of the disk samples lubricated with pure CD SAE 15W-40. Although numerous additives were included in CD SAE 15W-40, numerous pits, and debris were still observed, indicating that the wear for the CD SAE 15W-40 was severe. Machining textures also disappeared, suggesting the surface was polished, resulting in lower surface roughness ($R_a = 0.162 \mu\text{m}$) than that of the initial disk sample. With the addition of 3 wt.% BS in CD SAE 15W-40, numerous pits and debris, as well as plastic deformation and delamination regions (Fig. 4(g)), appeared, suggesting that BS particles promoted wear. When 3 wt.% BS + 0.5 wt.% TiF_3 or with 3 wt.% BS + 0.5 wt.% FeF_3 were added, machining textures and numerous smaller pits were observed ($R_a = 0.091 \mu\text{m}$), as shown in Fig. 4(h). Furthermore, evidence of the formation of a tribofilm (Fig. 4(i)) was also observed, as shown by the red oval ($R_a = 0.357 \mu\text{m}$). These results reveal that TiF_3 and FeF_3 provide an important contribution to the protection of frictional surfaces.

Table 2 shows the elemental composition of the worn areas lubricated with LP and CD SAE 15W-40. The carbon content of the wear zone lubricated with pure LP was 0.74% (Table 2(b)), induced most likely by contamination. Carbon content was increased to 21.49 wt.% (Table 2(c)), which indicated the participation of carbon in the tribofilm formation. When LP was added with 3 wt.% BS + 0.5 wt.% TiF_3 , carbon and titanium were both detected (Table 2(d)). This finding reveals that carbon and titanium again were an integral part of the tribofilm formation, which

supports a low friction coefficient. However, fluorine was not detected in BS-LP with 0.5 wt.% FeF₃, which may be due to the fact that the Fe peak closely approximates the F peak, which was also observed in EDS analysis [32].

With regard to the CD SAE 15W-40 with 3 wt.% BS + 0.5 wt.% TiF₃, in addition to phosphorus and sulfur, carbon and titanium were also detected as shown in Table 2(h), which again reveals that these elements participated in tribofilm formation.

Fig. 5 shows the Raman spectrum obtained at $\lambda_0 = 514$ nm from the wear regions of disk samples lubricated with LP and CD SAE 15W-40, with the test conditions all the same as Brunetto *et al.*'s [37]. The first-order carbon spectra generally exhibited two broad and strongly overlapping peaks with the intensity maxima at 1350 (D peak) and 1580 cm⁻¹ (G peak). The D peak (1350 cm⁻¹) was attributed to the disordered graphitic lattices, whereas the G peak (1580 cm⁻¹) to the ideal graphitic lattices [38]. Both peaks were not observed in the wear zones of LP and CD SAE15W-40 without 3 wt.% BS. However, both peaks were present when the lubricants were contaminated with 3 wt.% BS, and the location and I_D/I_G was different (not listed here). These results indicate that the BS particles had a role in reducing the both wear and friction reduction. The variations in location (Raman shift) and intensity of I_D/I_G suggest changes in the carbon structure of BS particles.

3.3 Characterization of the tribofilms

XPS was used to investigate the elemental chemical state of wear traces lubricated with different oil samples in order to sufficiently clarify the compositions of tribofilm of BS contaminated lubricants with TiF₃ or FeF₃.

Fig. 6 shows the elemental chemical valence state of the wear traces of the disk samples lubricated with 3 wt.% BS-LP with and without 0.5 wt.% TiF₃ or FeF₃. Fig. 6(a-c) shows the C_{1s} spectrum of the wear zones. In general, the peaks at 284.8 and 285.5 eV were attributed to C_{sp}² and C_{sp}³, respectively, and the peak at 288.9 eV belonged to C=O or O-C-O [39]. The C_{sp}² content (43.48%) of the wear zone lubricated with BS-LP was higher than that of the wear zones with TiF₃ (36.51%) or FeF₃ (16.67%). However, C_{sp}³ (15.38%) and C=O or O-C-O (1.92%) content were lower [40]. The variation in $I_{C_{sp2}}/I_{C_{sp3}}$ of wear zones lubricated with different oil samples are

shown in Table 2. The $I_{C_{sp2}}/I_{C_{sp3}}$ of the initial BS particles was 3.83. The $I_{C_{sp2}}/I_{C_{sp3}}$ of carbon on wear zones lubricated with BS-LP with and without TiF_3 or FeF_3 were 2.82, 1.85, and 0.41, respectively, which indicated that the tribofilm included some BS particles. The O_{1s} spectrum (Fig. 6(d-f)) of wear zones showed three peaks at 530.1, 531.3, and 532.5 eV, which belonged to metal oxide (labeled O1), C-O (labeled O2), and C=O (labeled O3), respectively. The metal oxide (12.91%) and C-O (15.21%) contents of the wear zone lubricated with BS-LP were higher than those of wear zones with TiF_3 (11.70% and 14.50%) or FeF_3 (3.84% and 8.25%). However, the C=O content (4.09%) was lower.

The Fe_{2p} spectra (Fig. 6(g, h)) of wear zones lubricated with BS-LP with and without TiF_3 were similar, showing two peaks at 710.9 and 724.6 eV. The first peak belongs to $Fe_{2p3/2}$, whereas the second peak belongs to $Fe_{2p1/2}$, indicating that Fe_2O_3 and Fe_3O_4 were present. The Fe_{2p} spectrum (Fig. 6(i)) of the wear zone lubricated with BS-LP with FeF_3 showed four peaks at 707, 710.9, 712.5, and 724.6 eV. The first peak was attributed to Fe atom, and the third peak was attributed to FeF_3 or FeF_2 [41], which is supported by the F_{1s} spectrum in Fig. 6(l). The peak at 684.9 eV was attributed to fluoride. The Ti_{2p} spectrum (Fig. 6(j)) of the wear zone lubricated with BS-LP with TiF_3 shows that the binding energies at 457.8 and 463.5 eV were the characteristic peaks of TiO_2 . The F_{1s} spectrum (Fig. 6(k)) shows that fluoride (684.9 eV) was present.

For the CD SAE 15W-40 tests, the C_{1s} and O_{1s} spectra of wear zones lubricated with different oil samples are shown in Fig. 7(a-f). Both C_{sp}^2 and C_{sp}^3 and group C=O or O-C-O content, as well as the contents of the oxygenated species on the surface of wear zones, show no regularity. These results were ascribed to the additives, which increased the species in the tribofilm. The $I_{C_{sp2}}/I_{C_{sp3}}$ of carbon on wear zones lubricated with BS contaminated CD SAE15W-40 with and without TiF_3 or FeF_3 were 1.60, 3.51, and 1.13, respectively, which again indicated a friction induced reaction that included BS contributing to the formation of the tribofilms [42].

Sulfur, phosphorus, titanium, and fluorine were detected when TiF_3 was added to BS contaminated CD SAE 15W-40. The S_{2p} spectrum (Fig. 7(k)) shows three peaks at 161.3, 162.5, and 168.7 eV. The binding energy at 161.3 eV belonged to FeS, whereas the binding energies at 162.5 and 168.7 eV belonged to FeS_2 [41]. The P_{2p} spectrum (Fig. 7(n)) showed only one peak at 133.2 eV, which was attributed to phosphate, derived from the antiwear additive. The Ti_{2p} spectrum (Fig. 7(m)) showed that the two peaks at 457.8 and 463.5 eV were the characteristic

peaks of TiO_2 .

Sulfur and fluorine were detected when FeF_3 was added to BS-CD SAE15W-40. The F_{1s} spectrum (Fig. 7(o)) shows that fluoride (684.9 eV) was present. The S_{2p} spectrum (Fig. 7(l)) showed only one peak at 169.1 eV, which belonged to the sulfates group. The antiwear and antifriction effects of BS-LP and engine lubricating oil were ascribed to the formation of a tribofilm that contained by carbon and fluorine.

3.4 Friction and wear mechanisms

In general, the formation of a lubrication film is determined by the composition and properties of the oil, and how these changes during the friction process. The active components in the oils can be physically adsorbed on the rubbing surfaces, and then these can be catalyzed to form a film. There will also be a physical adsorption role that can be proved indirectly via the variations in the elemental composition of the material on the frictional surfaces. This was the case when the upper and lower samples were immersed in the LP and CD SAE -15W-40 at 70 °C for 2 h. **Table 4** includes both the elements of Ti and F that were detected on the surface of the frictional pairs when TiF_3 was added into LP with and without BS particles. This supports the argument that TiF_3 was physically adsorbed on to the surfaces. For the CD SAE 15W-40, neither P or Zn was detected, only S on the surface of disk friction pair material when 3% BS was added into CD SAE 15W-40. However, the elements of S, P and F were detected when TiF_3 were added into lubricant. These results also indicated TiF_3 was easily adsorbed on the frictional surfaces.

XPS results indicated that the different compounds (such as TiO_2 and iron oxides) were detected on the surface of frictional pairs, which was ascribed to the frictional driven chemical reactions. During the rubbing process, the tribo-chemical reactions associated with wear were critical to film formation as shown in Fig. 4(d) and lots of chemical bonds formed on the wear regions as described in Antusch's work [19]. This phenomenon can be used to explain the antiwear and antifriction mechanisms of BS-LP and TiF_3 . The appearance of TiO_2 and fluoride on the surface of wear zones of the disks indicated that the decomposition of TiF_3 resulted in a low friction coefficient [32]. Regarding BS-LP with FeF_3 , although the tribofilm contained fluoride, BS agglomeration and iron oxides resulted in a high friction coefficient, similar to the mechanisms observed in [43].

In the fully formulated CD SAE 5W-40, the various additives including ZDDP contributed to the formation of more robust tribofilms than those that were formed with LP, resulting in lower mass loss due to wear and lower friction coefficient. It is well known that ZDDP contributes to the formation of protective films, however the addition of the TiF_3 , and FeF_3 has also been shown to adsorb on to the tribo-surfaces, forming a protective film and preventing the BS from contacting these surfaces. The increased friction coefficient of lubrication with 0.5 wt.% FeF_3 was ascribed to the formation of iron oxides (Fig. 7 (i)) and sulfates (Fig. 7 (l)), forming agglomerates with the BS particles. There was also some evidence that the FeF_3 derived tribological film of was incomplete.

In all, adsorption and tribo-chemical reactions were two very important factors leading to the reduction of both friction and wear in BS contaminated LP and CD SAE 15W-40 when catalyzed by TiF_3 and FeF_3 particles. The simple schematic diagram of wear and friction mechanisms when TiF_3 and FeF_3 are used is shown in Fig.8. However, tribofilms containing carbon, titanium and fluorine from the TiF_3 and BS particles were more robust than those of the tribofilms formed from the FeF_3 and BS particles in lubricating oils. The reason for this being that TiO_2 was better than iron oxides for reducing wear [44].

4 Conclusions

A systematic series of tribological experiments have been conducted with the goal of establishing a method for the design of engine lubricants to mitigate against the effects of soot contamination. A Titanium and an Iron inorganic fluoride based additive system, was developed and added to both a base oil (liquid paraffin) and a fully formulated engine lubricant (CD SAE 15W-40), both when contaminated with soot derived from bio-fuel. The resulting tribofilms were characterized and the formation mechanisms discerned. The following conclusions can be drawn:

- (1) Both TiF_3 and FeF_3 efficiently enhanced the antiwear properties of LP and CD SAE 15W-40 lubricants when contaminated with biofuel soot of 3 wt% BS. Using TiF_3 as the catalyst led to a larger friction reduction compared to FeF_3 .
- (2) The tribofilms were formed of carbon, titanium, iron, and fluorine, once the inorganic fluorides had been added into the BS contaminated lubricating oils.
- (3) The structure of the BS particles within the observed wear zones was modified, as a result of

frictional rubbing.

- (4) The formation of robust tribofilms for the BS contaminated LP and CD SAE 15W-40 with TiF_3 or FeF_3 particles was driven by adsorption and tribo-chemical reactions.

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Tables

Table 1 Physicochemical properties of liquid paraffin and CD SAE 15W-40

Item	Liquid paraffin	CD SAE15W-40	Methods
Density (kg/m ³ , 20 °C)	880	850	ASTM D4052
Kinematical viscosity (mm ² /s, 40 °C)	100	110.6	ASTM D445
Viscosity index	98	142	ASTM D2270
Sulfur content (wt%)	No	2.5%	ASTM D4294
Phosphorus content (wt%)	No	0.1%	ASTM D1091
Water (m/m) %	Trace	Trace	ASTM D6304
Pour point (°C)	−15	−24	ASTM D9
Flash point (°C)	210	220	ASTM D93
Acid number (mgKOH g ^{−1})	0.014	0.035	ASTM D664

Table 2 EDS analysis of wear zones of bottom samples lubricated with LP and CD SAE 15W-40

Symbol	Element contents (wt%)										
	C	O	Fe	Zn	Ti	Mg	Si	S	P	Mn	Cr
a	-	7.99	88.29	-	-	-	2.63	-	-	1.10	-
b	0.74	-	94.83	-	-	-	3.52	-	-	0.91	-
c	21.49	9.35	64.95	-	-	-	3.14	-	-	1.06	-
d	1.22	5.85	85.44	-	0.87	-	4.78	-	-	0.57	1.28
e	1.26	8.43	85.56	-	-	-	4.57	-	-	0.27	-
f	0.31	7.83	85.33	0.46	-	1.65	2.19	0.86	0.61	0.75	-
g	0.56	5.85	88.19	-	-	-	3.59	0.28	0.13	0.94	0.26
h	0.98	9.31	84.20	-	0.02	0.64	4.45	0.36	0.10	-	-
i	1.05	4.23	90.04	0.09	-	-	3.84	0.08	0.67	-	-

Note: (a) Initial, (b) LP, (c) LP+3 wt%BS, (d) LP+3 wt%BS+0.5 wt% TiF₃, (e) LP+3 wt%BS+0.5 wt%FeF₃, (f) CD SAE 15W-40, (g) CD SAE 15W-40+3 wt%BS, (h) CD SAE 15W-40+3 wt%BS+0.5 wt%TiF₃, (i) CD SAE 15W-40+3 wt%BS+0.5 wt% FeF

Table 3 Carbon atom contents of wear zones lubricated with LP and fully formulated engine oil

Item	Element atom content (at%)			
	C(sp ²)	C(sp ³)	C=O (O-C-O)	I _{sp2} /I _{sp3}
BS	46.79	12.23	1.97	3.83
LP+3wt% BS	43.48	15.38	1.92	2.82
LP+3wt% BS+0.5wt% TiF ₃	36.51	19.72	2.82	1.85
LP+3wt% BS+0.5wt% FeF ₃	16.67	39.81	6.39	0.41

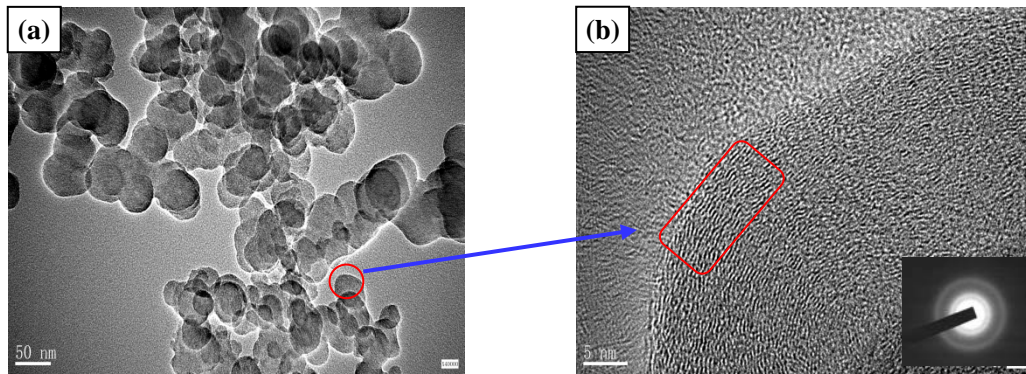
CD SAE 15W-40+3wt% BS	34.10	21.22	3.66	1.60
CD SAE 15W-40+3wt% BS+0.5wt% TiF ₃	41.36	11.78	1.98	3.51
CD SAE 15W-40+3wt% BS+0.5wt FeF ₃	31.90	24.23	2.1	1.31

Table 4 The surface active element contents of bottom material after static immersion at 70 °C for 2 h

Items	Element content (wt%)									
	C	O	Fe	Cr	Mn	Si	P	S	Ti	F
a	0.36	-	94.06	0.27	1.31	4.0	-	-	-	-
a+0.5wt% TiF ₃	1.01	13.75	11.90	-	-	1.33	-	-	18.01	54.0
a+3wt%BS	2.57	6.46	85.12	-	-	5.85	-	-	-	-
a+3wt%BS+0.5 wt% TiF ₃	-	9.90	53.81	-	-	2.77	-	-	5.32	28.2
b	1.27	6.84	86.31	0.43	1.42	3.14	0.6	-	-	-
b+3wt%BS	14.57	1.47	79.3	0.66	1.53	1.99	0.57	-	-	-
b+0.5wt% TiF ₃	0.46	-	47.71	0.54	23.9	1.10	1.84	15.4		2.20
b+3wt%BS+0.5 wt% TiF ₃	0.71	-	93.06	0.17	0.93	4.17	0.24	0.71	-	-

a: LP; b: CD SAE 15W-40

Figures



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Fig. 1. Morphology and distribution diagram of BS average particle diameter: (a) morphology, (b) diffraction pattern, and (c) distribution diagram of BS particles

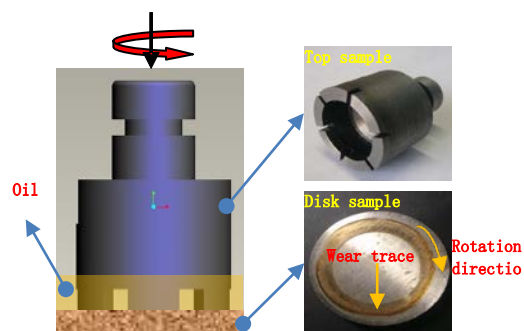


Fig. 2. Schematic diagrams of friction pairs of end-face tribometer

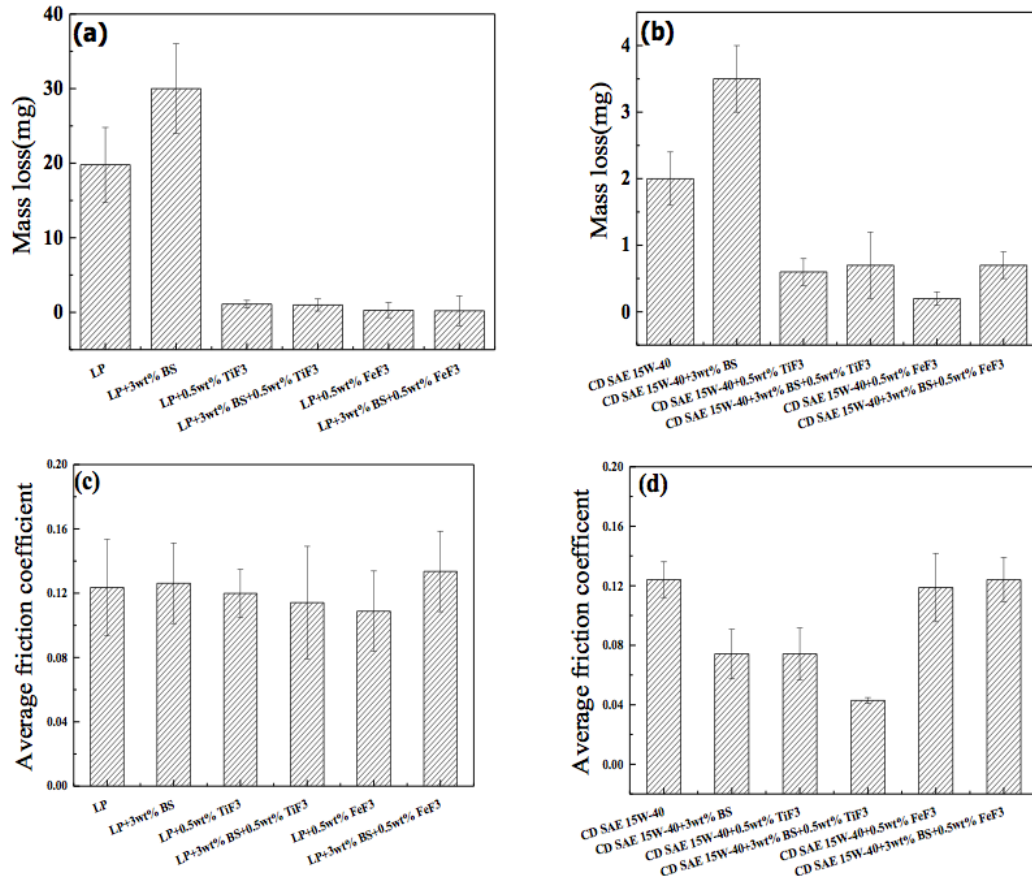
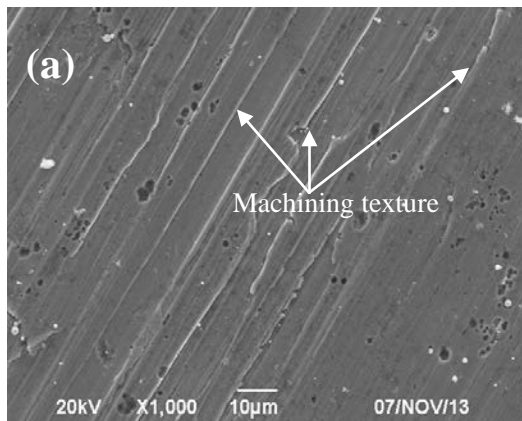
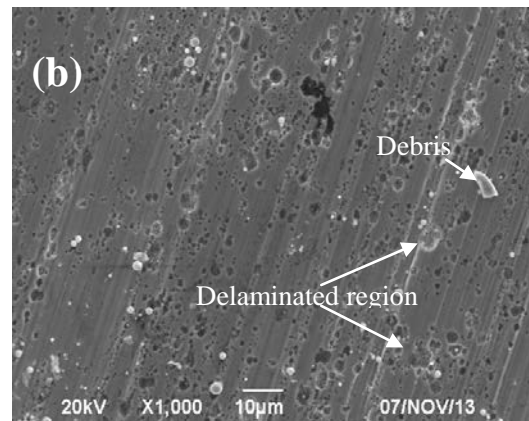


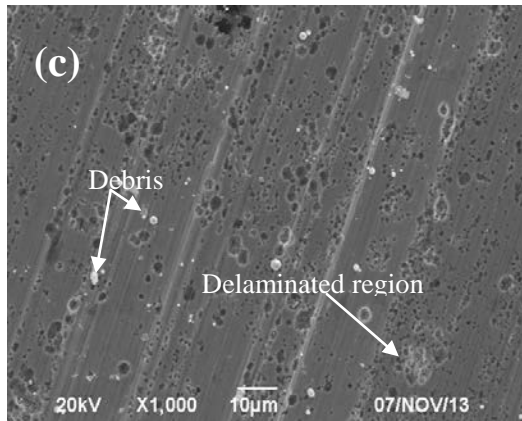
Fig. 3. Mass loss and average friction coefficient variations of 3 wt.% BS contaminated LP and CD SAE 15W-40 with and without 0.5 wt.% TiF_3 or FeF_3 at 1500 N and rotation speed of 294 rpm for 60 min: (a) &(c) LP, and (b)&(d) CD SAE-15W-40



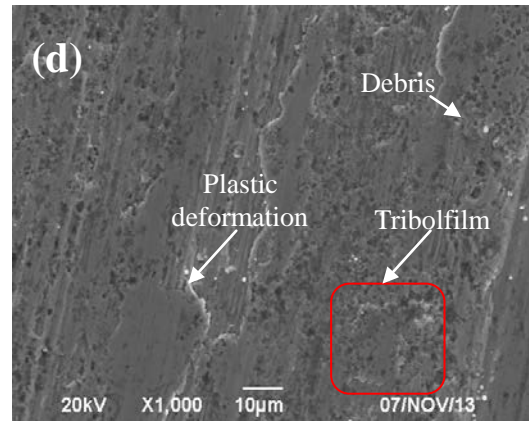
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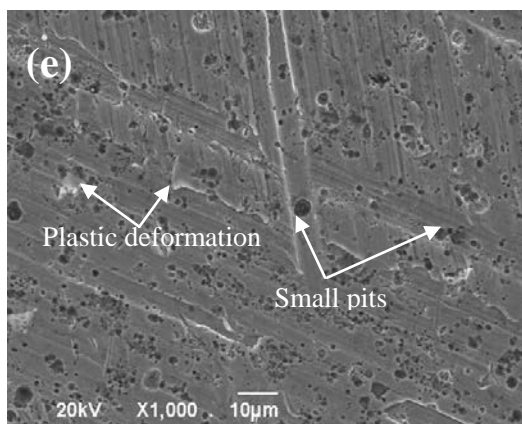
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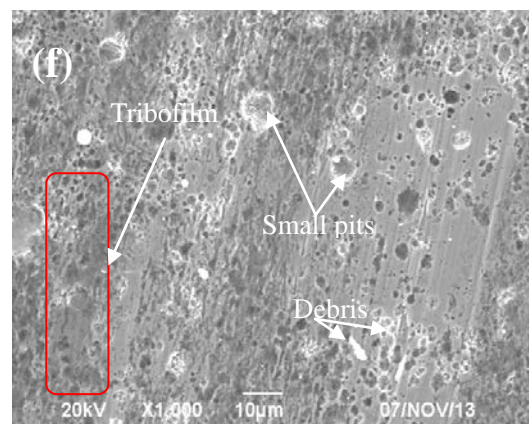
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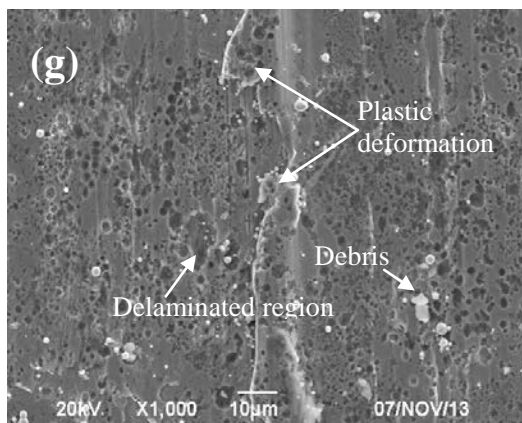
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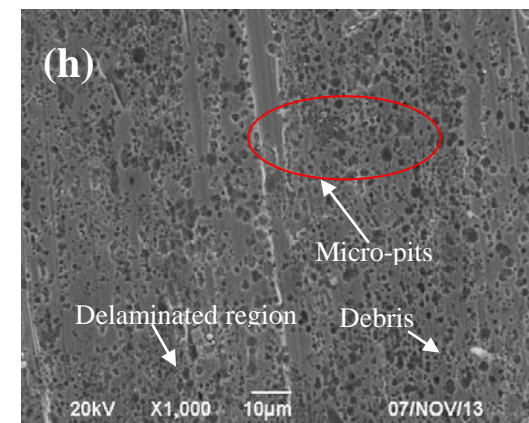
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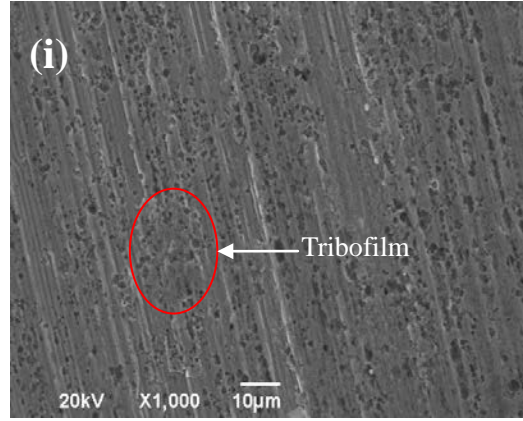
$R_a=0.162\mu\text{m}$



$R_a=0.344\mu\text{m}$



$R_a=0.091\mu\text{m}$



$$R_a=0.357\mu\text{m}$$

Fig. 4. SEM images and variations of the wear zones of bottom samples lubricated with LP and CD SAE 15W-40: (a) initial, (b) LP, (c) LP + 3 wt.% BS, (d) LP + 3 wt.% BS + 0.5 wt.% TiF_3 , (e) LP + 3 wt.% BS + 0.5 wt.% FeF_3 , (f) CD SAE 15W-40, (g) CD SAE 15W-40+3 wt.% BS, (h) CD SAE 15W-40 + 3 wt.% BS + 0.5 wt.% TiF_3 , and (i) CD SAE 15W-40 + 3 wt.% BS + 0.5 wt.% FeF_3

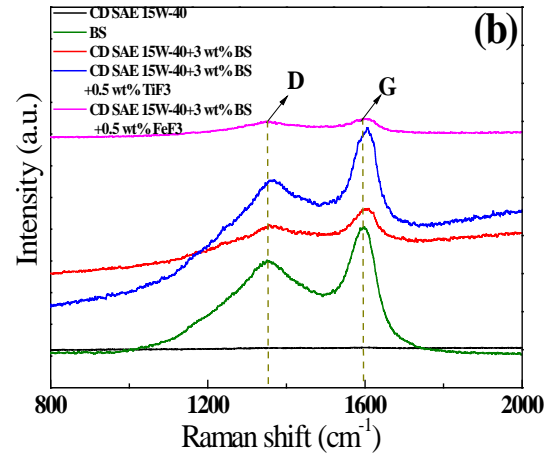
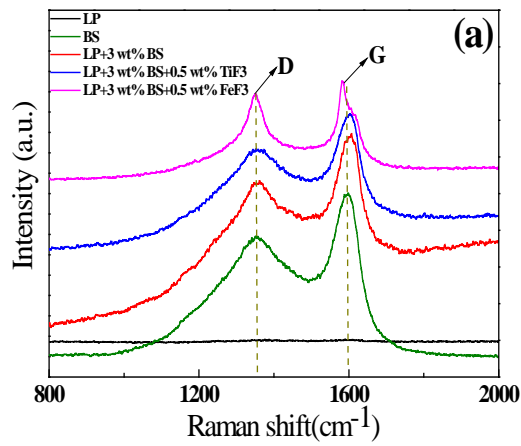


Fig. 5. Raman spectroscopy of wear zones lubricated with LP and CD SAE 15W-40: (a) LP, and (b) CD 15W-40

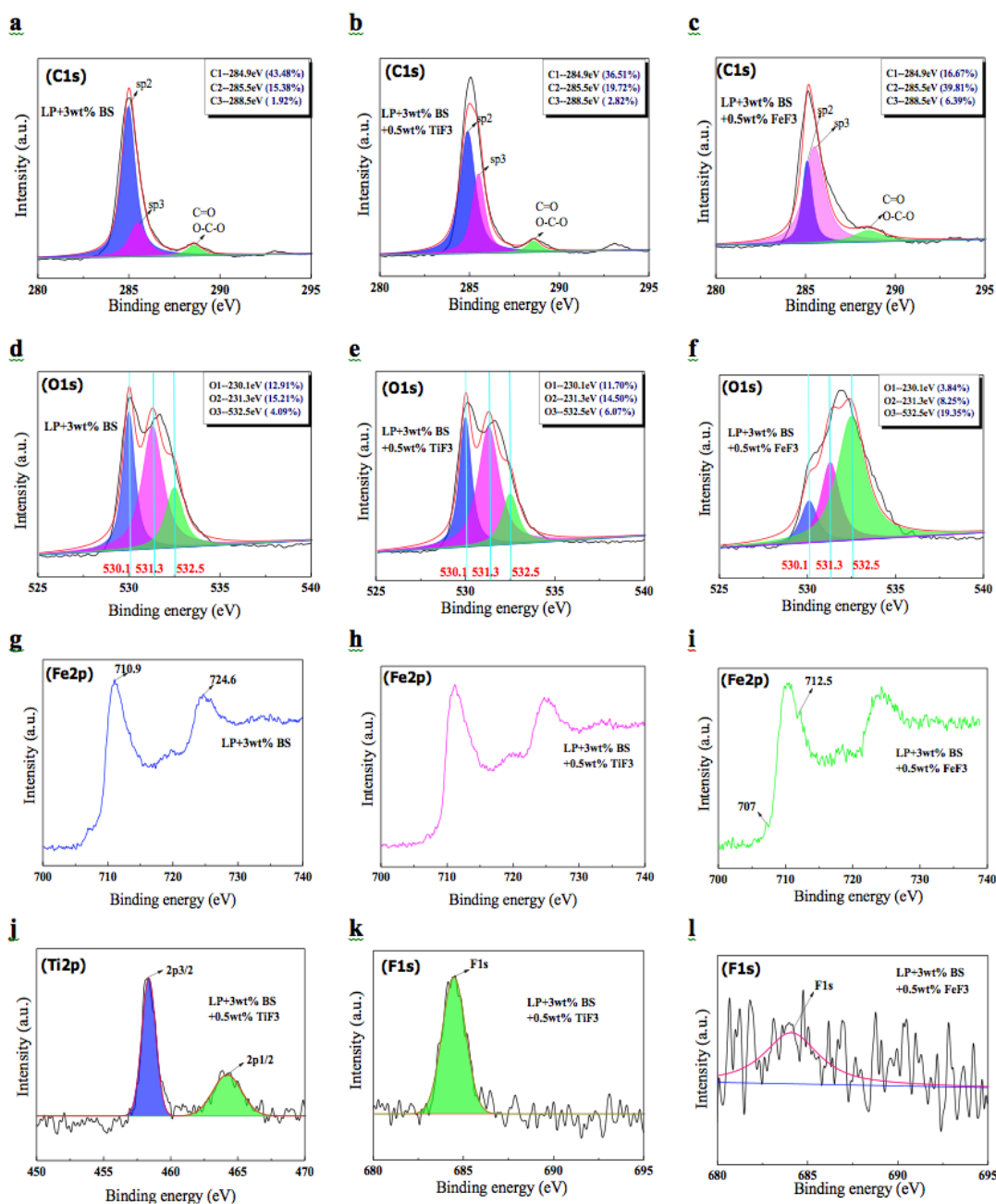


Fig. 6. Elemental chemical valence state of wear regions lubricated with 3 wt.% BS-contaminated LP with and without 0.5 wt.% TiF₃ or FeF₃

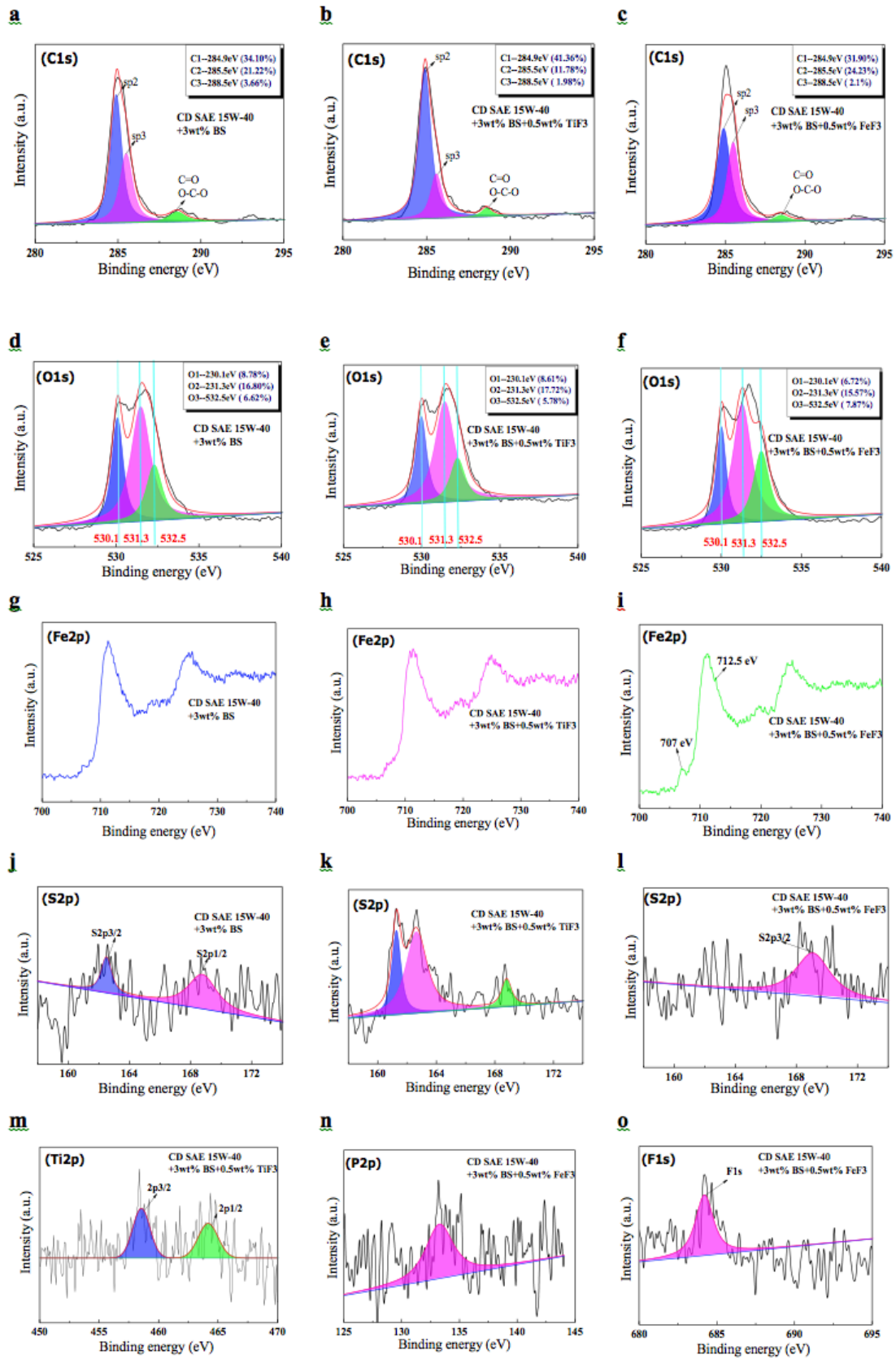


Fig.7. Element chemical valence state of wear regions lubricated with 3wt% BS contaminated CD SAE 15W-40 with and without 0.5 wt.% TiF_3 or FeF_3

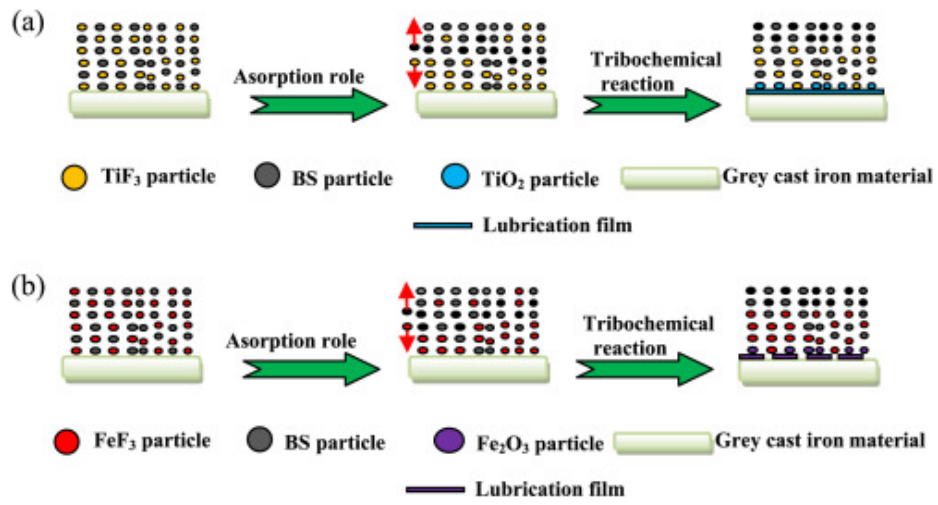


Fig. 8. Schematic diagrams of wear and friction mechanisms of TiF_3 and FeF_3 particles